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THE CHEMISTRY OF O,N-DIARYLHYDROXYLAMINES - I

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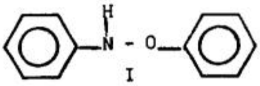
REARRANGEMENTS from the nitrogen atom of many N-substituted anilines into the aromatic ring are known[1]. Among these, the rearrangement of hydrazobenzene to benzidine is intramolecular and requires diprotonation of the substrate[2], while the acid-catalyzed conversion of N-phenylhydroxylamine to o- and p-aminophenol is intermolecular and requires monoprotonation of the substrate[3]. The theoretical interest of these reactions has promoted us to attempt the synthesis of O,N-diphenylhydroxylamine, (I), in order to investigate its behavior under acidic conditions.



I

Protonation of I might lead to a Π-complex similar to those

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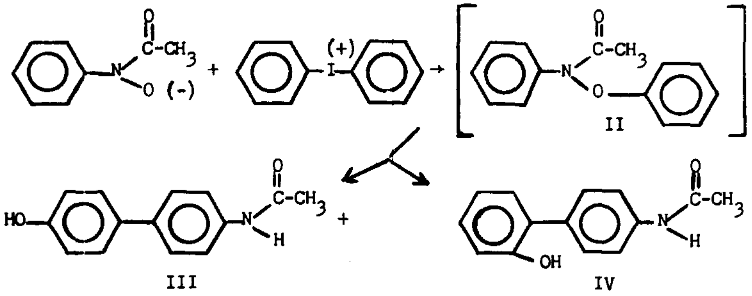
[1] G. S. Wheland, "Advanced Organic Chemistry", 3rd Edition, John Wiley and Sons, Inc., New York, 1960, pp. 648-662.

[2] C. A. Bunton, C. K. Ingold and M. M. Mhala, J. Chem. Soc., 1957, 1906.

[3] H. E. Heller, E. D. Hughes and C. K. Ingold, Nature, 168, 909 (1951).

proposed for the benzidine rearrangement[4,5,6] and for the rearrangement of *p*-quinamines[7]; the expected products of such reaction would be, *inter alia*, aminohydroxybiphenyls. Alternatively, protonation might result in fragmentation. Products of this pathway might be aminophenols, aminodiphenyl ethers, etc., in addition to aminohydroxybiphenyls[3].

Beringer and coworkers have shown that diphenyliodonium salts are effective phenylating agents for organic and inorganic bases under mild conditions[8]. A reasonable synthetic route appeared to be phenylation of the anion of N-acetyl-N-phenylhydroxylamine[9] to afford (II), followed by saponification to I.



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[4] M. J. S. Dewar, "Electronic Theory of Organic Chemistry", Oxford Press, London, 1949, pp. 235-240; "Kekulé Symposium on Theoretical Organic Chemistry", Butterworths Scientific Publications, London, 1958, pp. 198 ff.

[5] L. C. Snyder, *J. Am. Chem. Soc.*, *84*, 340 (1962).

[6] G. S. Hammond and J. S. Clovis, *Tetrahedron Letters*, *1962*, 945.

[7] B. Miller, *Tetrahedron Letters*, *1962*, 55.

[8] (a) F. M. Beringer, A. Brierly, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Am. Chem. Soc.*, *75*, 2708 (1953); (b) F. M. Beringer and E. M. Gindler, *ibid.*, *77*, 3203 (1955); (c) F. M. Beringer, P. S. Forgione and M. G. Yudis, *Tetrahedron*, *8*, 49 (1960).

[9] E. Bamberger, *Ber.*, *51*, 637 (1918).

Addition of N-acetylphenylhydroxylamine to a scrupulously deoxygenated aqueous solution of diphenyliodonium hydroxide in equimolar ratio produced a solution which remained colorless, but from which there separated over a period of 2 days at 25° a partially solid, red-brown precipitate. The aqueous solution was decanted and the precipitate dried under vacuum at 25°. Iodobenzene was recovered from the trap, and a red-brown solid remained. Fractional crystallization of the solid from chloroform yielded 33% of 4-hydroxy-4'-acetylamino-biphenyl, (III), and some of a compound that we formulate as its isomer, (IV), on the basis of the following evidence.

The melting point of III, 226° (reported, 224-5° [10]) was identical with that of an authentic sample prepared by acetylation[10] of the amine synthesized by the method of Bamberger[11], and a mixed melting point of the two was undepressed. The O,N-diacetyl amines were similarly identical; m.p. and m.m.p. 222-223.5° (reported, 219-220[12]). A mixed melting point of III and the O,N-diacetyl amine was depressed to 188-189°. The infrared spectrum of III showed maxima at 3340 cm.$^{-1}$, 1660 cm.$^{-1}$ and 1580 cm.$^{-1}$, and was superimposable upon that of the authentic material.

The melting point of the compound formulated as IV, 196-197°, agrees with the reported value, 198-199° [12]. The infrared spectrum was very similar to that of III, showing maxima at 3330 cm.$^{-1}$, 1660^{-1} and 1580^{-1}, but differing from it slightly in the fingerprint region.

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[10] L. C. Raiford and E. P. Clark, J. Am. Chem. Soc., 48, 483 (1926).

[11] E. Bamberger, Ann., 443, 196 (1925).

[12] C. Finzi, Gazz. chim. ital., 61, 33 (1931).

Since the conditions for the workup were very mild with respect to temperature and were chosen so as to avoid acidic catalysts, it seemed probable that the rearranged products were formed under the reaction conditions and were not formed by rearrangement during the workup. This interpretation was confirmed by the fact that the infrared spectrum of the crude product mixture was identical with that of a mixture of the purified products. Since the reaction mixture never became more acidic than pH 7 during the entire course of the reaction, and since any of the expected intermediates should be very weakly basic, it is very unlikely that a proton-catalyzed process is involved.

We propose as a likely explanation of these results that the anion of N-acetylphenylhydroxylamine is indeed phenylated by the diphenyliodonium ion, affording II, which spontaneously rearranges intramolecularly to the observed products III and IV. To test the possibility of reaction by mechanisms involving phenol or phenoxide ions, we have demonstrated that diphenyliodonium hydroxide is relatively stable in the absence of the hydroxamic acid by following the disappearance of hydroxide ions. After 2 days at 25° only 3.3% of the diphenyliodonium hydroxide had decomposed to phenol, diphenyl ether and iodobenzene[13], far less than the amount required to explain the yield of III and IV, unless phenoxide ion were involved in a polar chain mechanism for which

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[13] "Diphenyliodonium bromide. . .with hydroxide ion in water gives a small amount of phenol and a large amount of diphenyl ether, presumably formed by further reaction of the initially formed phenol"[8a].

only a catalytic amount of free phenoxide was necessary[14].

The alternative pathway for formation of III and IV directly from diphenyliodonium ion and the hydroxamic acid anion through a Π-complex cannot at present be ruled out. Intermolecular pathways for rearrangement of II to III and IV are, however, unattractive to us on the basis of the present evidence.

If II is indeed formed, its lability may be rationalized by considering that the role of the first proton required by the benzidine rearrangement may be taken by the electron-withdrawing acetyl group, while the function of the second proton may be partially fulfilled by the greater electronegativity of oxygen *vis-à-vis* nitrogen[15].

Further investigations of this reaction and of others in this series are in progress. It is particularly to be noted that the biphenyl derivatives found as products of the decomposition of phenylhydroxylamine and of phenyl azide in the presence of phenol[3] could be thought to arise by intramolecular, acid-catalyzed rearrangement of I formed initially in the reaction.

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[14] We acknowledge the suggestion of this alternative, intermolecular pathway by Professor Jack Hine, to whom we are grateful for helpful discussions.

[15] The Π-complex postulated as an intermediate in the benzidine rearrangement has frequently been assumed to be monoprotonated in spite of the kinetic order in acid, since the products obtained from unsymmetrical hydrazobenzenes are more easily rationalized on this basis[4] and molecular orbital calculations predict a greater likelihood of existence of such a structure[5].